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(56) Documents cited

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(58) Field of search

CSD

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(54) Cellulase enzyme detergent composition

(57) A detergent composition for clothes contains: (a) at least one surfactant selected from anionic surfactants, nonionic surfactants and

ampholytic surfactants and (b) bacteria- and/or fungi-derived cellulase having the enzyme activity of at least 100 units for cotton cloths (1 unit is the activity for 1 g of sample to form 1 mμ mole of reducing sugar from a cotton cloth in one minute).

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SPECIFICATION

Detergent composition

The present invention relates to a detergent composition. More particularly, the present invention relates to a detergent composition for clothing which contains a specific surfactant and a specific cellulase as essential ingredients.

A remarkable progress has been made recently in washing of clothing items. In other words, the development of feedstocks suitable for detergents, the improvement of water quality, the improvement and diffusion of washing machines, and the improvement of fibers have made the washing of clothing items very easy. Especially, the improvement of feedstocks for detergents is remarkable. The improvement of surfactants, builders, dispersants, fluorescent dyes, and bleaching agents gives one an impression that the detergent compositions for clothing items have almost reached completion. However, the development of detergents for clothing items has been backed up by the technical ideas which are summarized below. (1) To cause dirt to separate from fibers physicochemically by causing dirt and/or fiber surface to adsorb a surfactant and builder, whereby lowering the interfacial tension between dirt and/or fiber and water. (2) To disperse and solubilize dirt with a surfactant and inorganic builder. (3) To decompose dirt chemically with an enzyme such as protease. (4) To bleach stains with a bleaching agent. (5) To carry out whitening by causing fiber surfaces to adsorb a fluorescent dye. (6) To prevent, using a chelating agent, the ingredients effective for washing from being precipitated by divalent metal ions.

Conventionally, the fundamental idea of producing a detergent for clothing items was directed to how to incorporate effectively a detergent with an ingredient which attacks dirt directly or an auxiliary which helps such an ingredient to attack dirt. At the present time, detergent compositions based on such a fundamental idea have reached a point where no more improvement cannot be made in washing performance and great efforts would be required to increase washing power further.

In order to develop a new detergent composition from a new standpoint free from established ideas about washing of clothing items, the present inventors carried out a series of intensive studies, which unexpectedly led to the findings that when a detergent composition is incorporated with a specific cellulase in combination with a specific surfactant, it exhibits an outstanding washing effect for dirt which seems to have nothing to do with the enzyme activity of the cellulase.

As mentioned above, using an enzyme is known in the art of detergents. There are known only those enzymes which act effectively on specific dirt. For instance, a protease for dirt caused by protein, an amylase for dirt caused by starch, and a lipase for dirt caused by oil and fat. These enzymes attack dirt directly, whereas the cellulase in this invention acts in a different way. Although the washing mechanism of the cellulase is not elucidated completely yet, presumably it acts on the fiber surfaces, particularly of cotton or cotton mixing, rather than on dirt, causing the fiber to swell or peeling the thin skin of the top layer of the fiber together with dirt. Further, it is presumed that the new fiber surface with dirt removed is covered by the specific surfactant and is protected from re-contamination with dirt.

The dirt that sticks to clothing items includes inorganic solids like mud as well as various kinds of dirt derived from proteins, oils and fats, starch, coloring matters, sweat, etc. combined together. On oxidation and other change, dirt takes on various states. Especially, a remarkable variety of dirt is observed on babies' and children's clothes. In addition, collars, cuffs, and socks become dirty with dirt characteristic of their owns. Such being the case, there has been a strong desire for the appearance of a general-purpose detergent having an outstanding washing power.

45 Detailed description of the invention

It is an object of the present invention to provide, in answer to the above-mentioned requirement, a general-purpose, powerful detergent for clothing items. The detergent of this invention is based on the findings that the combination of a specific cellulase and a specific surfactant exhibits an outstanding washing effect for any kind of dirt on cotton-containing cloths.

The present invention relates to a detergent composition for clothing items which contains as essential ingredients (a) at least one kind of surfactant selected from the group consisting of anionic surfactant, nonionic surfactant, and ampholytic surfactant, (b) bacteria- and/or fungi-derived cellulase having the enzyme activity of at least 100 units for cotton cloths. In this specification, 1 unit is defined as the activity for 1 g of sample to form 1 mμ mole of reducing sugar from cotton fabric in one minute.

The cellulase as an essential ingredient of the detergent composition of this invention is limited to one which has the activity for insoluble cellulose, particularly cotton cloths. According to the present art, the enzyme activity of cellulase is represented simply by the ability to hydrolyze water-soluble arts, the enzyme activity of cellulase is represented simply by the ability to hydrolyze water-soluble cellulose (for CMCase) and the ability for hydrolyze insoluble cellulose (for Avicelase). They are not sufficient to represent the characteristics of the enzyme activity of the cellulase in this invention. Thus, the present inventors devised the above-mentioned unique method for representation of activity. It is not clear, however, how such representation of activity is related with CMCase and Avicelase. In any way, it was found that a certain type of cellulase which has an enzyme activity higher than a certain level for cotton cloths acts effectively on dirt on clothing items.

The cellulase used as an essential ingredient in this invention is limited to one which is derived from bacterial or fungi. As known well, cellulase exists in nature and is widely distributed in fungi, bacteria, animals, and plants. It was found, however, that the cellulase derived from animals and plants is not so effective for the purpose intended in this invention as the cellulase derived from bacteria and fungi.

According to the present invention, the detergent composition should contain the cellulase derived from bacteria and fungi in such an amount that the enzyme activity for cotton cloths is 100 units/g or higher, preferably, 500 units/g or higher at the optimal pH.

The enzyme activity of cellulase for cotton cloths was determined as follows: A test liquid composed of 200 mg of cotton cloth cut into small pieces to facilitate stirring, 10 mg of cellulase sample, and 10 cc of aqueous buffer solution of the pH optimal for the cellulase activity was stirred at 40°C for 20 hours, and the liberated reducing sugar was determined according to the DNS method. The activity for 1 g of cellulase sample to form 1 μ mole of reducing sugar in 1 minute was defined as 1 unit. (The cotton cloth sample has a viscometric degree of polymerization of at least 1000 and has a crystalline structure of cellulose I as determined by the X-ray method). According to the DNS method, the color which is generated when 3,5-dinitrosalicylic acid is reacted with the reducing group of a sugar while boiling in an alkali is determined colorimetrically. (For more detail, refer to "Experiments on Biochemistry, Part I, Determination of Reducing Sugar", by Sakuzo Fukui, P. 19, 1969, published by Gakkai Shuppan Center).

The term "optimal pH" as used in the method for determination means the range of pH in which each cellulase exhibits its maximum activity.

The specific surfactant which is another essential ingredient of the detergent composition of this invention is an anionic surfactant, nonionic surfactant, or ampholytic surfactant. Cationic surfactants and long-chain fatty acid salts are not preferable. It was found by the present inventors that the activity of cellulase (for insoluble cellulose having a viscometric degree of polymerization greater than 1000 and having an X-ray crystallographical structure of cellulose I) is hindered by cationic surfactants and long-chain fatty acid salts. However, it was also found that the combination of a specific surfactant and a specific cellulase as mentioned above results in no deteriorating effect on the cellulase activity or exhibits a synergistic action more than offset deteriorating effects. The present inventors completed this invention based on these findings.

One great advantage of the detergent composition of this invention is that it is very useful to improve the washing power of detergent compositions containing phosphate builder as well as detergent compositions containing none or a small quantity of phosphate builder. A phosphate has been in general use because it is effective to remove dirt of minute mud particles which have entered the space between fibers. In order to avoid eutrophication, the content of phosphate in detergents tends to be decreased, or the production of detergents containing phosphate is being regulated by law. Thus, it has become very difficult to wash out mud dirt by using detergents of recent production. It is well known that such detergents can hardly wash out mud dirt which has entered a cotton cloth. Thus, washing mudded cotton canvas shoes is a headache for housewives. The detergent composition of this invention will solve such a problem. The detergent composition of this invention will exhibit a washing power equal to or superior to a weak alkaline powder detergent containing a sufficient quantity of phosphate in washing of mudded cotton cloths or cotton mixing cloths, when it is used (1) in combination with an alkaline detergent containing none or a small quantity of phosphate or (2) in combination with a weak alkaline or neutral liquid detergent containing no phosphate.

Another advantage of the detergent composition of this invention is that it enhances the whitening effect of a fluorescent dye, apart from the enzyme activity of cellulase. A fluorescent dye is the most effective whitening agent, and the effective use of this expensive compound has been proposed in many forms. Among others, a variety of chemicals which increase the adsorption of fluorescent dye by clothing items in the washing bath have been proposed. Such an attempt to increase the adsorption of a fluorescent dye is successful in a simple system consisting of a fluorescent dye and an adsorption promoter, but is not so successful in a complex multi-component system. Actually, effective adsorption promoters are not available at present. The whiteness of clothing imparted by a fluorescent brightening treatment is lost gradually as the fluorescent dye is lost by washing. To replenish such a loss, a fluorescent dye is incorporated into detergents for clothing items. Any compound which improves the dyeability of a fluorescent dye in repeated washing cycles is very important from a practical point of view. However, such a compound has not been found so far. The detergent composition of this invention exhibits a synergistic whitening effect of cellulase and fluorescent dye. The mechanism of such a synergistic effect is not elucidated completely. It is presumed that cellulase acts on cellulose fibers to make the fiber surface more receptive to fluorescent dyes.

Further, another great advantage of the detergent composition of this invention is that when the cellulase is used in combination with a bleaching agent, the washing and bleaching effect is improved synergistically for general-purpose washing.

As mentioned above, using an enzyme in the technical field of washing and bleaching agents is known, but the known enzymes are limited to those which are effective for specific types of dirt. For

instance, a protease is known as effective for stains caused by protein, an amylase, for stains caused by starch, and a lipase, for stains caused by oils and fats. These enzymes attack dirt and stains directly. The cellulase used in the detergent composition of this invention is one of hydrolases like protease and amylase; nevertheless, it exhibits a remarkable washing effect for the dirt which is not at all associated with the enzyme activity of cellulase. It is particularly suitable for washing out inorganic solid dirt.

Dirt and stains on clothing items are not simple. They are complex mixtures of inorganic solid dirt, feed-derived proteins and oils and fats, and secretions, which are often oxidized with time. Therefore, they are not necessarily washed out completely even when a cellulase is added to the washing liquid.

In the studies on improvement of washability by the use of cellulase, the present inventors found that the object is achieved when the cellulase is combined with a bleaching agent. Such a combination provides a synergistic washing-bleaching effect.

Another great advantage of the detergent composition of this invention is that complex dirt and stains can be washed out economically and effectively if the cellulase is combined with at least one kind of enzyme selected from the group consisting of carboxylate ester hydrazine, glucoside hydrazine, and peptidyl peptide hydrazine which are hydrolases other than cellulase.

Complex dirt and stains on collars, cuffs, and socks are sticking firmly to fibers, and it was difficult to wash them out using conventional detergents. The present inventors found that if cellulase is combined with other enzymes (particularly protease, amylase, and lipase), complex dirt and stains can be washed out economically and effectively with a superior washing power. This is because the protease, amylase, and lipase attack directly proteins, oils and fats, and starch, respectively, and the cellulase performs its own washing action.

Another great advantage of the detergent composition of this invention is that the washing performance for inorganic dirt is not affected by the pH of the detergent composition. As known well, an enzyme exhibits its maximum enzyme activity at its optimal pH. However, the detergent composition of this invention using the cellulase having an optimal pH in the acid region exhibits the sufficient washing performance even in the alkaline region. The detergent composition of this invention was not different from conventional detergents in the effect of strength of fibers to be washed.

Another great advantage of the detergent composition of this invention is that it can be used in any form of detergents, e.g., spray-dried powder, spray-cooled powder, blended powder, tablets, and liquid.

As mentioned above, any cellulase widely distributed in bacteria and fungi and purified fractions thereof can be used as the cellulase which is an essential ingredient of the detergent composition of this invention.

Examples of bacteria and fungi which produce cellulase are as follows:

(a) Bacteria

- (1) *Bacillus hydrolyticus*,
- (2) *Cellulobacillus mucosus*,
- (3) *Cellulobacillus myxogenes*,
- (4) *Cellulomonas* sp.,
- (5) *Cellvibrio fulvus*,
- (6) *Cellulivibrio vulgaris*,
- (7) *Clostridium thermocellulaseum*,
- (8) *Clostridium thermocellum*,
- (9) *Corynebacterium* sp.,
- (10) *Cytophaga globulosa*,
- (11) *Pseudomonas fluorescens* var. *cellulosa*,
- (12) *Pseudomonas solanacearum*,
- (13) *Bacterioides succinogenes*,
- (14) *Ruminococcus elbus*,
- (15) *Ruminococcus flavefaciens*,
- (16) *Sorandium* composition,
- (17) *Butyrivibrio*,
- (18) *Clostridium* sp.,
- (19) *Xanthomonas cyamopsideis*,
- (20) *Sclerotium bataticola*,
- (21) *Bacillus* sp.,
- (22) *Thermoactinomyces* sp.,
- (23) *Actinobifida* sp.,

(b—l) Fungi (Actinomycetes)

- (1) *Actinomycetes* sp.,
- (2) *Streptomyces* sp.,

(b—II) Fungi (Mould: Deuteromycetes, Phycmycetes, Ascomycetes)

	(1) <i>Arthrobotrys superba</i> ,	
	(2) <i>Aspergillus aureus</i> ,	
5	(3) <i>Aspergillus flavipes</i> ,	5
	(4) <i>Aspergillus flavus</i> ,	
	(5) <i>Aspergillus fumigatus</i> ,	
	(6) <i>Aspergillus luchuensis</i> ,	
	(7) <i>Aspergillus nidulans</i> ,	
10	(8) <i>Aspergillus niger</i> ,	10
	(9) <i>Aspergillus oryzae</i> ,	
	(10) <i>Aspergillus rugulosus</i> ,	
	(11) <i>Aspergillus sydwi</i> ,	
	(12) <i>Aspergillus tamarii</i> ,	
15	(13) <i>Aspergillus terreus</i> ,	15
	(14) <i>Aspergillus unguis</i> ,	
	(15) <i>Aspergillus ustus</i> ,	
	(16) <i>Takamine-Cellulase</i> ,	
	(17) <i>Aspergillus saitoi</i> ,	
20	(18) <i>Botrytis cinerea</i> ,	20
	(19) <i>Botryodiplodia theobromae</i> ,	
	(20) <i>Cladosporium cucumerinum</i> ,	
	(21) <i>Cladosporium herbarum</i> ,	
	(22) <i>Coccospora agricola</i> ,	
25	(23) <i>Curvularia lunata</i> ,	25
	(24) <i>Chaetomium thermophile</i> var. <i>coprophile</i> ,	
	(25) <i>Chaetomium thermophile</i> var. <i>dissitum</i> ,	
	(26) <i>Sporotrichum thermophile</i> ,	
	(27) <i>Taromyces emersonii</i> ,	
30	(28) <i>Thermoascus aurantiacus</i> ,	30
	(29) <i>Humicola grisea</i> var. <i>thermoidea</i> ,	
	(30) <i>Humicola insolens</i> ,	
	(31) <i>Malbranchea pulchella</i> var. <i>suifurea</i> ,	
	(32) <i>Myriococcum albomyces</i> ,	
35	(33) <i>Stilbella thermophile</i> ,	35
	(34) <i>Torula thermophila</i> ,	
	(35) <i>Chaetomium globosum</i> ,	
	(36) <i>Dictyostelium discoideum</i> ,	
	(37) <i>Fusarium</i> sp.,	
40	(38) <i>Fusarium bulbigenum</i> ,	40
	(39) <i>Fusarium equiseti</i> ,	
	(40) <i>Fusarium lateritium</i> ,	
	(41) <i>Fusarium lini</i> ,	
	(42) <i>Fusarium oxysporum</i> ,	
45	(43) <i>Fusarium vasinfectum</i> ,	45
	(44) <i>Fusarium dimerum</i> ,	
	(45) <i>Fusarium japonicum</i> ,	
	(46) <i>Fusarium scirpi</i> ,	
	(47) <i>Fusarium solani</i> ,	
50	(48) <i>Fusarium moniliforme</i> ,	50
	(49) <i>Fusarium roseum</i> ,	
	(50) <i>Helminthosporium</i> sp.,	
	(51) <i>Memnoniella echinata</i> ,	
	(52) <i>Humicola fucoatra</i> ,	
55	(53) <i>Humicola grisea</i> ,	55
	(54) <i>Monilia sitophila</i> ,	
	(55) <i>Monotospora brevis</i> ,	
	(56) <i>Mucor pusillus</i> ,	
	(57) <i>Mycosphaeella citrullina</i> ,	
60	(58) <i>Myrothecium verrucaria</i> ,	60
	(59) <i>Papulaspora</i> sp.,	
	(60) <i>Penicillium</i> sp.,	
	(61) <i>Penicillium capsulatum</i> ,	
	(62) <i>Penicillium chrysogenum</i> ,	
65	(63) <i>Penicillium frequentans</i> ,	65
	(64) <i>Penicillium janthinellum</i> ,	

	(65) <i>Penicillium luteum</i> ,	
	(66) <i>Penicillium piscarium</i> ,	
	(67) <i>Penicillium soppi</i> ,	
5	(68) <i>Penicillium spinulosum</i> ,	5
	(69) <i>Penicillium turbatum</i> ,	
	(70) <i>Penicillium digitatum</i> ,	
	(71) <i>Penicillium expansum</i> ,	
	(72) <i>Penicillium pusillum</i> ,	
	(73) <i>Penicillium rubrum</i> ,	
10	(74) <i>Penicillium wortmanii</i> ,	10
	(75) <i>Penicillium variable</i> ,	
	(76) <i>Pestalotia palmarum</i> ,	
	(77) <i>Pestalotiopsis westerdijkii</i> ,	
	(78) <i>Phoma</i> sp.,	
15	(79) <i>Schizophyllum commune</i> ,	15
	(80) <i>Scopulariopsis brevicaulis</i> ,	
	(81) <i>Rhizopus</i> sp.,	
	(82) <i>Sporotrichum carnis</i> ,	
	(83) <i>Sporotrichum pulnosum</i> ,	
20	(84) <i>Stachybotrys atra</i> ,	20
	(85) <i>Torula</i> sp.,	
	(86) <i>Trichoderma viride</i> ,	
	(87) <i>Trichurus cylindricus</i> ,	
	(88) <i>Verticillium albo-atrum</i> ,	
25	(89) <i>Aspergillus cellulosa</i> ,	25
	(90) <i>Penicillium glaucum</i> ,	
	(91) <i>Cunninghamella</i> sp.,	
	(92) <i>Mucor mucedo</i> ,	
	(93) <i>Rhizopus chinensis</i> ,	
30	(94) <i>Coremiella</i> sp.,	30
	(95) <i>Karlingia rosea</i> ,	
	(96) <i>Phytophthora cactorum</i> ,	
	(97) <i>Phytophthora citricola</i> ,	
	(98) <i>Phytophthora parasitica</i> ,	
35	(99) <i>Pythium</i> sp.,	35
	(100) <i>Saprolegniaceae</i> ,	
	(101) <i>Ceratocystis ulmi</i> ,	
	(102) <i>Chaetomium globosum</i> ,	
	(103) <i>Chaetomium indicum</i> ,	
40	(104) <i>Neurospora crassa</i> ,	40
	(105) <i>Sclerotium rolfsii</i> ,	
	(106) <i>Aspergillus</i> sp.,	
	(107) <i>Chrysosporium lignorum</i> ,	
	(108) <i>Penicillium notatum</i> ,	
45	(109) <i>Pyricularia oryzae</i> ,	45
	(b—III) Fungi (Basidiomycetes)	
	(1) <i>Collybia velutipes</i> ,	
	(2) <i>Coprinus sclerotigenus</i> ,	
	(3) <i>Hydnum henningsii</i> ,	
50	(4) <i>Irpex lacteus</i> ,	50
	(5) <i>Polyporus sulphureus</i> ,	
	(6) <i>Polyporus betreus</i> ,	
	(7) <i>Polystictus hirsutus</i> ,	
	(8) <i>Trametes vitata</i> ,	
55	(9) <i>Irpex consolis</i> ,	55
	(10) <i>Lentinus lepideus</i> ,	
	(11) <i>Poria vaporaria</i> ,	
	(12) <i>Fomes pinicola</i> ,	
	(13) <i>Lenzites styracina</i> ,	
60	(14) <i>Merulius lacrimans</i> ,	60
	(15) <i>Polyporus palustris</i> ,	
	(16) <i>Polyporus annosus</i> ,	
	(17) <i>Polyporus versicolor</i> ,	
	(18) <i>Polystictus sanguineus</i> ,	

- | | | |
|---|---|---|
| 5 | (19) <i>Poria vallantii</i> ,
(20) <i>Puccinia graminis</i> ,
(21) <i>Tricholoma fumosum</i> ,
(22) <i>Tricholoma nudum</i> ,
(23) <i>Trametes sanguinea</i> ,
(24) <i>Polyporus schweinitzii</i> FR.,
(25) <i>Conidiophora cerebella</i> , | 5 |
|---|---|---|

According to the present invention, the following commercial cellulases which are derived from the above bacteria and fungi can be used for the detergent composition.

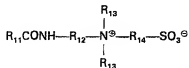
- | | | |
|----|--|----|
| 10 | (1) Cellulase AP (Amano Pharmaceutical Co., Ltd.)
(2) Cellulosin AP (Ueda Chemical Co., Ltd.)
(3) Cellulosin AC (Ueda Chemical Co., Ltd.)
(4) Cellulase-Onozuka (Kinki Yakult Seizo Co., Ltd.)
(5) Pancellase (Kinki Yakult Seizo Co., Ltd.) | 10 |
| 15 | (6) Macerozyme (Kinki Yakult Seizo Co., Ltd.)
(7) Meicelase (Meiji Seika Kaisha, Ltd.)
(8) Celluzyme (Nagase Co., Ltd.)
(9) Soluble sclase (Sankyo Co., Ltd.)
(10) Sanzyme (Sankyo Co., Ltd.) | 15 |
| 20 | (11) Cellulase A-12-C (Takeda Chemical Industries, Ltd.)
(12) Toyo-Cellulase (Toyo Jozo Co., Ltd.)
(13) Driserase (Kyowa Hakko Kogyo Co., Ltd.)
(14) Lulzyme (Luipold Werk)
(15) Takamine-Cellulase (Chemische Fabrik) | 20 |
| 25 | (16) Wallerstein-Cellulase (Sigma Chemicals)
(17) Cellulase Type I (Sigma Chemicals)
(18) Cellulase Serva (Serva Laboratory)
(19) Cellulase 36 (Rohm and Haas)
(20) Miles Cellulase 4,000 (Miles) | 25 |
| 30 | (21) R & H Cellulase 35, 36, 38 conc (Philip Morris)
(22) Combizym (Nysco Laboratory)
(23) Cellulase (Makor Chemicals)
(24) Cellucrust (NOVO Industry)
(25) Cellulase (Gist-Brocades) | 30 |

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|----|--|----|
| 35 | The anionic, nonionic, and amphotolytic surfactants used for the detergent composition of this invention are exemplified as follows: | 35 |
|----|--|----|

- | | | |
|-----------|---|----|
| 10 to 16. | (1) Linear or branched alkylbenzenesulfonates having alkyl groups of an average carbon number of 10 to 16. | |
| 40 | (2) Alkyl or alkenyl ether sulfates having linear or branched alkyl groups or alkenyl groups of an average carbon number of 10 to 20, and having 0.5 to 8 moles on an average of ethylene oxide, propylene oxide, butylene oxide, ethylene oxide/propylene oxide=0.1/9.9 to 9.9/0.1, or ethylene oxide/butylene oxide=0.1/9.9 to 9.9/0.1 added in one molecule. | 40 |
| 10 to 20. | (3) Alkyl or alkenyl sulfates having alkyl groups or alkenyl groups of an average carbon number of 10 to 20. | |
| 45 | (4) Olefinsulfonates having 10 to 20 carbon atoms on an average in one molecule.
(5) Alkanesulfonates having 10 to 20 carbon atoms on an average in one molecule. | 45 |
| 50 | The counter ions of the anionic surfactants are exemplified by alkali metal ions such as sodium and potassium; alkaline earth metal ions such as calcium and magnesium; ammonium ion; and alkanolamines (e.g., monoethanolamine, diethanolamine, triethanolamine, and triisopropanolamine) having 1 to 3 alkanol groups of carbon number 2 or 3. | 50 |

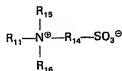
(6) Sulfonate-type amphotolytic surfactants represented by the following formulas:

No. 1



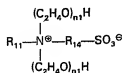
(where R_{11} is an alkyl or alkenyl group of carbon number 8 to 24; R_{12} is an alkylene group of carbon number 1 to 4; R_{13} is an alkyl group of carbon number 1 to 5; and R_{14} is an alkylene or hydroxyalkylene group of carbon number 1 to 4).

No. 2



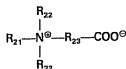
(where R_{11} and R_{14} are defined as above; R_{15} and R_{16} are an alkyl or an alkenyl group of carbon number 8 to 24 or 1 to 5, respectively).

No. 3



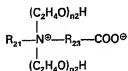
- 5 (where R_{11} and R_{14} are defined as above; and $n1$ is an integer of 1 to 20.
(7) Betaine-type ampholytic surfactants represented by the following formulas:

No. 1



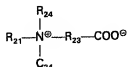
- (where R_{21} is an alkyl, alkenyl, β -hydroxyalkyl, or β -hydroxyalkenyl group of carbon number 8 to 24; R_{22} is an alkyl group of carbon number 1 to 4; and R_{23} is an alkylene or hydroxyalkylene group of carbon number 1 to 6).

No. 2

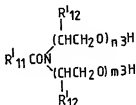


(where R_{21} and R_{23} are defined as above; and n_2 is an integer of 1 to 20).

No. 3



- (where R_{21} and R_{23} are defined as above; and R_{24} is a carboxyalkyl or hydroxyalkyl group of carbon number 2 to 5).
(8) Polyoxyethylene alkyl or alkenyl ethers having alkyl or alkenyl groups of an average carbon number 10 to 20 and having 1 to 20 moles of ethylene oxide added.
(9) Polyoxyethylene alkyl phenyl ethers having alkyl groups of an average carbon number 6 to 12 and having 1 to 20 moles of ethylene oxide added.
(10) Polyoxypropylene alkyl or alkenyl ethers having alkyl groups or alkenyl groups of an average carbon number 10 to 20 and having 1 to 20 moles of propylene oxide added.
(11) Polyoxybutylene alkyl or alkenyl ethers having alkyl groups of alkenyl groups of an average carbon number 10 to 20 and having 1 to 20 moles of butylene oxide added.
(12) Nonionic surfactants having alkyl groups or alkenyl groups of an average carbon number 10 to 20 and having 1 to 30 moles in total of ethylene oxide and propylene oxide or ethylene oxide and butylene oxide added (the molar ratio of ethylene oxide to propylene oxide or butylene oxide being 0.1/9.9 to 9.9/0.1).
(13) Higher fatty acid alkanolamides or alkylene oxide adducts thereof represented by the formula:



(where R'₁₁ is an alkyl group or alkenyl group of carbon number 10 to 20; R'₁₂ is H or CH₃; n3 is an integer of 1 to 3; and m3 is an integer of 0 to 3).

(14) Sugar fatty acid esters composed of sugar and fatty acid of an average carbon number 10 to 20.

(15) Fatty acid glycerine monoesters composed of glycerine and fatty acid of an average carbon number 10 to 20.

(16) Alkylamine oxides represented by the formula:



(where R'₁₃ is an alkyl group or alkenyl group of carbon number 10 to 20; and R'₁₄ and R'₁₅ are alkyl groups of carbon number 1 to 3).

The detergent composition of this invention may contain optionally the following ingredients as required.

I. Cellulase derived from animals and plants listed below

(a) Protozoa (ciliata, flagellata, amoeba, etc.)

- (1) Endopodinium neglectum
(2) Trichomonas termopsisidus

(b) Mollusc (snail, soft clam, shipworm, etc.)

- (1) Helix pomatia
(2) Stromonas gligas
(3) Dolabella auricula Solander
(4) Mytilus Ostrea
(5) Xylophaga dorsalis
(6) Cryptochiton stelleri
(7) Pterocera crocata
(8) Caelatura hauteoauri ruellani
(9) Melanoides tuberculata
(10) Mya arenaria
(11) Mactra solidissima
(12) Bankia setacea
(13) Bankia indica
(14) Teredo
(15) Modiola modiolus
(16) Cryptoplax japonica
(17) Heliotis japonica
(18) Turbo cornutus
(19) Tegula pheifferi
(20) Lamintina Imbricata
(21) Fasciolaria trapezium
(22) Dolabella auricula
(23) Homolodoris japonica
(24) Dendrodoris rubra var. nigromaculata
(25) Onchidium verruculatum
(26) Euhadra peliomphala
(27) Mytilus edulis
(28) Meretrix meretrix lusoria
(29) Venerupis philippinarum
(30) Octopus sp.

(c) Nematoda

- (1) Ditylenchus destructor
(2) Ditylenchus dipsaci

(d) Annelida

- (1) Eunice aphroditois
(2) Tylosrhynchus heterochaetus
(3) Glycera chlrori
(4) Loimia medusa

	(5) <i>Sabellastarte indica</i>	
	(6) <i>Rhizodrilus</i> sp.	
	(7) <i>Pheretina</i> sp.	
	(e) Echinodermata (sea chestnut etc.)	
5	(1) <i>Anthodiaris crassispina</i>	5
	(2) <i>Pseudocentrotus depressus</i>	
	(3) <i>Hemicentrotus pulcherrimus</i>	
	(4) <i>Psammechinus milians</i>	
	(f) Crustacea	
10	(1) <i>Mitella mitella</i>	10
	(2) <i>Megallia exotica</i>	
	(3) <i>Calappa lophus</i>	
	(4) <i>Gaeidea depressus</i>	
15	(5) <i>Pachygrapsus crassipes</i>	15
	(6) <i>Plagusia dentipes</i>	
	(7) <i>Charybdis miles</i>	
	(8) <i>Carcinoplax longimanus</i>	
	(9) <i>Tiarinia cornigera</i>	
	(10) <i>Leptomithrax edwardsi</i>	
20	(11) <i>Naxioides hystrix</i>	20
	(12) <i>Hepalogaster dentata</i>	
	(13) <i>Aniculus aniculus</i>	
	(14) <i>Dardanus crassimanus</i>	
	(15) <i>Upogebia major</i>	
25	(16) <i>Panulirus japonicus</i>	25
	(17) <i>Penaeus japonicus</i>	
	(18) <i>Scyllarides sieboldi</i>	
	(19) <i>Procambarus clarkii</i>	
	(g) Insects (ants, beetles, etc.)	
30	(1) <i>Termes obesus</i>	30
	(2) <i>Ctenolepisma lineata</i>	
	(3) <i>Cerambyx cerdo</i>	
	(4) <i>Xestobium refovillosum</i>	
	(5) <i>Nasutitermes excruciosus</i>	
35	(6) <i>Coptotermes lacteus</i>	35
	(7) <i>Stromatium fulvum</i>	
	(8) <i>Dixippus morosus</i>	
	(9) <i>Limnoria lignorum</i>	
	(h) Algae	
40	(1) <i>Cladophora rupestris</i>	40
	(2) <i>Ulva lactuca</i>	
	(3) <i>Laminaria digitata</i>	
	(4) <i>Rhodomenia palmata</i>	
	(i) Lichenes	
45	(1) <i>Usneaceae</i>	45
	(2) <i>Cladoniaceae</i>	
	(3) <i>Parmeliaceae</i>	
	(4) <i>Umbilicariaceae</i>	
	(j) Terrestrial chlorophytes	
50	(1) Tobacco plant	50
	(2) Pineapple stalks	
	(3) <i>Acer pseudoplatanus</i> stalks	
	(4) Bush bean leaves	
	(5) Swiss chard	
55	(6) Spinach	55
	(7) <i>Solanum dulcamara</i> root	
	(8) Pumpkin	
	(9) <i>Asparagus</i> tip	
	(10) Barley	
60	(11) Malt	60

II. Hydrolase except cellulase

Carboxylate ester hydrolase, thioester hydrolase, phosphate monoester hydrolase, and phosphate diester hydrolase which act on the ester bond; glycoside hydrolase which acts on glycosyl compounds; an enzyme that hydrolyzes N-glycosyl compounds; thioether hydrolase which acts on the ether bond; and α -amino-acyl-peptide hydrolase, peptidyl-amino acid hydrolase, acyl-amino acid hydrolase, dipeptide hydrolase, and peptidyl-peptide hydrolase which act on the peptide bond. Preferable among them are carboxylate ester hydrolase, glycoside hydrolase, and peptidyl-peptide hydrolase.

These preferably hydrolases are exemplified as follows:

(1) Proteases belonging to peptidyl-peptide hydrolase

Pepsin, pepsin B, rennin, trypsin, chymotrypsin A, chymotrypsin B, elastase, enterokinase, cathepsin C, papain, chymopapain, ficin, thrombin, fibrinolysin, renin, subtilisin, aspergillopeptidase A, collagenase, clostridiopeptidase B, kallikrein, gastrisin, cathepsin D, bromelain, keratinase, chymotrypsin C, pepsin C, aspergillopeptidase B, urokinase, carboxypeptidase A and B, and aminopeptidase.

(2) Glycoside hydrolases

Cellulase which is an essential ingredient is excluded from this group. α -amylase, β -amylase, gluco amylase, invertase, lysozyme, pectinase, chitinase, and dextranase. Preferable among them are α -amylase and β -amylase. They function in acid to neutral systems, but one which is obtained from bacteria exhibits high activity in an alkaline system.

(3) Carboxylate ester hydrolase

Carboxyl esterase, lipase, pectin esterase, and chlorophyllase. Especially effective among them is lipase.

Trade names of commercial products and producers are as follows: "Alkalase", "Esperase", "Sabinase", "AMG", "BAN", "Fungamill", "Sweetzyme", "Termamill" (Novo Industry, Copenhagen, Denmark); "Maksatase", "High-alkaline protease", "Amylase THC", "Lipase" (Gist Brocades, N.V., Delft, Holland); "Protease B-400", "Protease B-4000", "Protease AP", "Protease AP 2100" (Schweizerische Ferment A.G., Basel, Switzerland); "CRD Protease" (Monsanto Company, St. Louis, Missouri, U.S.A.); "Placase" (Piopln Corporation, Monticello, Illinois, U.S.A.); "Pronase P", "Pronase AS", "Pronase AF" (Kaken Chemical Co., Ltd., Japan); "Laplase P-2000" (Lapidas, Secran, France); protease products (Tyler standard sieve, 100% pass 16 mesh and 100% on 150 mesh) (Clington Corn Products (Division of Standard Brands Corp., New York); "Takamine", "Bromelain 1:10", "HT Protease 200", "Enzyme L-W" (obtained from fungi, not from bacteria) (Miles Chemical Company, Elkhart, Ind., U.S.A.); "Rozyne P-11 Conc.", "Pectinol", "Lipase B", "Rozyne PF", "Rozyne J-25" (Rohm & Haas, Philadelphia, U.S.A.); "Ambrozyme 200" (Jack Wolf & Co., Ltd., Subsidiary of Nopco Chemical Company, Newark, N.J., U.S.A.); "ATP 40", "ATP 120", "ATP 160" (Lapidas, Secran, France); "Orpase" (Nagase & Co., Ltd., Japan).

The hydrolase other than cellulase is incorporated into the detergent composition as much as required according to the purpose. It should preferably be incorporated in an amount of 0.001 to 5 wt%, more preferably 0.02 to 3 wt%, in terms of purified one. This enzyme should be used in the form of granules made of crude enzyme alone or in combination with other components in the detergent composition. Granules of crude enzyme are used in such an amount that the purified enzyme is 0.001 to 5 wt%. Purified enzyme is diluted so that the granules are used in an amount of 0.002 to 10 wt%, preferably 0.1 to 5 wt%.

III. Cationic surfactants and long-chain fatty acid salts

1) saturated or unsaturated fatty acid salts of an average carbon number 10 to 24 in the molecule,

2) alkyl or alkenyl ether carboxylic acid salts containing an alkyl or alkenyl group of an average carbon number 10 to 20 and having 0.5—8 mol on an average of ethylene oxide, propylene oxide, butylene oxide, ethylene oxide/propylene oxide in a ratio of 0.1:9.9 to 9.9:0.1 or ethylene oxide/butylene oxide in a ratio of 0.1:9.9 to 9.9:0.1 added in one molecule,

3) α -sulfofatty acid salts or esters of the following formula:



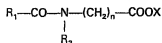
wherein Y represents an alkyl group of carbon number 1 to 3 or a counter ion, Z represents a counter ion, and R represents an alkyl or alkenyl group of carbon number 10 to 20,

4) amino acid-type surfactants of the following general formula:



wherein R_1 represents an alkyl or alkenyl group of carbon number 8 to 24, R_2 represents a hydrogen or an alkyl group of carbon number 1 to 2, R_3 represents an amino acid residue and X represents an alkali metal or alkaline earth metal ion,

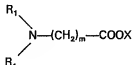
No. 2



5 wherein R_1 , R_2 and X have the same meaning as above and n represents an integer of 1—5.

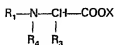
5

No. 3



wherein R_1 and X have the same meaning as above and m represents an integer of 1—8,

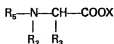
No. 4



10 wherein R_1 , R_3 and X have the same meaning as above and R_4 represents hydrogen or an alkyl or hydroxyalkyl of carbon number 1 to 2,

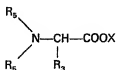
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No. 5



wherein R_2 , R_3 and X have the same meaning as above and R_5 represents a β -hydroxyalkyl or β -hydroxyalkenyl group of carbon number 6 to 28, and

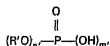
No. 6



15 wherein R_2 , R_3 and X have the same meaning as above,
5) phosphate ester surfactants:

15

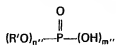
No. 1 alkyl (or alkenyl) acid phosphates of the general formula:



wherein R' represents an alkyl or alkenyl group of carbon number 8 to 24, $n'+m'=3$ and $n'=1-2$,

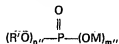
20 No. 2 alkyl (or alkenyl) phosphates of the general formula:

20



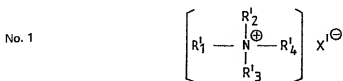
wherein R' has the same meaning as above, $n''+m''=3$ and $n''=1-3$, and

No. 3 alkyl (or alkenyl) phosphates of the general formula:

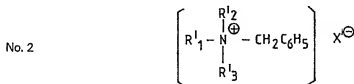


25 wherein R' , n'' and m'' have the same meaning as above and M represents Na, K or Ca, and
6) cationic surfactants of the following general formula

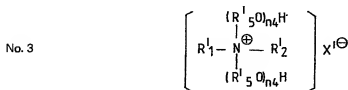
25



wherein at least one of R_1' , R_2' , R_3' and R_4' represents an alkyl or alkenyl group of carbon number 8 to 24 and the others represent an alkyl group of carbon number 1 to 5, and X' represents a halogen,



5 wherein R_1' , R_2' , R_3' and X' have the same meaning as above,



wherein R_1' , R_2' and X' have the same meaning as above, R_5' represents an alkylene group of carbon number 2 to 3 and n_4 represents an integer of 1—20.

IV. Builders

10 [1] Divalent sequestering agents

The composition may contain 0—50 wt% of one or more builder components selected from the group consisting of alkali metal salts and alkanolamine salts of the following compounds:

1) phosphates such as orthophosphate, pyrophosphate, triphosphosphate, metaphosphate, hexametaphosphate and phytic acid,

2) phosphonates such as ethane-1,1-diphosphonate, ethane-1,1,2-triphosphonate, ethane-1-hydroxy-1,1-diphosphonate and its derivatives, ethanehydroxy-1,1,2-triphosphonate, ethane-1,2-dicarboxy-1,2-diphosphonate and methanehydroxy-phosphonate,

3) phosphonocarboxylates such as 2-phosphonobutane-1,2-dicarboxylate, 1-phosphonobutane-2,3,4-tricarboxylate and α -methylphosphonosuccinate,

4) salts of amino acids such as aspartic acid, glutamic acid and glycine,

5) aminopolyacetates such as nitrilotriacetate, ethylenediaminetetraacetate, diethylenetriaminepentaacetate, iminodiacetate, glycol ether diamine tetraacetate, hydroxyethyliminodiacetate and dienolate,

6) high molecular electrolytes such as polyacrylic acid, polyacetic acid, polyitaconic acid,

polycitraconic acid, polyfumaric acid, polymaleic acid, polymesaconic acid, poly- α -hydroxyacrylic acid,

polyvinylphosphonic acid, sulfonated polymaleic acid, maleic anhydride/diisobutylene copolymer,

maleic anhydride/styrene copolymer, maleic anhydride/methyl vinyl ether copolymer, maleic

anhydride/ethylene copolymer, maleic anhydride/ethylene crosslinked copolymer, maleic

anhydride/vinyl acetate copolymer, maleic anhydride/acrylonitrile copolymer, maleic anhydride/acrylic

ester copolymer, maleic anhydride/butadiene copolymer, maleic anhydride/isoprene copolymer, poly- β -

ketocarboxylic acid derived from maleic anhydride and carbon monoxide, itaconic acid/ethylene

copolymer, itaconic acid/acetic acid copolymer, itaconic acid/maleic acid copolymer, itaconic

acid/acrylic acid copolymer, malonic acid/methylene copolymer, mesaconic acid/fumaric acid

copolymer, ethylene glycol/ethylene terephthalate copolymer, vinylpyrrolidone/vinyl acetate

copolymer, 1-butene-2,3,4-tricarboxylic acid/itaconic acid/acrylic acid copolymer, polyester

polyaldehydocarboxylic acid containing quaternary ammonium group, cis-isomer of epoxysuccinic acid,

poly[N,N-bis(carboxymethyl)acrylamide], poly(hydroxycarboxylic acid), starch/succinic acid or maleic

acid or terephthalic acid ester, starch/phosphoric acid ester, dicarboxystarch, dicarboxymethylstarch

and cellulose/succinic acid ester,

7) non-dissociating polymers such as polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone

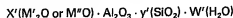
and cold water-soluble, urethanated polyvinyl alcohol,

8) salts of dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic

- acid, pimelic acid, suberic acid, azelaic acid and decane-1,10-dicarboxylic acid; salts of diglycolic acid, thiodiglycolic acid, oxalacetic acid, hydroxydisuccinic acid, carboxymethylhydroxysuccinic acid and carboxymethyltartronic acid; salts of hydroxycarboxylic acids such as glycolic acid, malic acid, hydroxypivalic acid, tartaric acid, citric acid, lactic acid, gluconic acid, mucic acid, glucuronic acid and dialdehydestarch oxide; salts of itaconic acid, methylsuccinic acid, 3-methylglutaric acid, 2,2-dimethylmalonic acid, maleic acid, fumaric acid, glutamic acid, 1,2,3-propanetricarboxylic acid, aconitic acid, 3-butene-1,2,3-tricarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, ethanetetracarboxylic acid, ethenetetracarboxylic acid, n-alkenylaconitic acid, 1,2,3,4-cyclopentanetetracarboxylic acid, phthalic acid, trimelic acid, hemimellitic acid, pyromellitic acid, benzenehexacarboxylic acid, tetrahydrofuran-1,2,3,4-tetracarboxylic acid and tetrahydrofuran-2,2,5,5-tetracarboxylic acid; salts of sulfonated carboxylic acids such as sulfoitaconic acid, sulfoftricarballic acid, cysteic acid, sulfoacetic acid and sulfosuccinic acid; carboxymethylated sucrose, lactose and raffinose, carboxymethylated pentaerythritol, carboxymethylated gluconic acid, condensates of polyhydric alcohols or sugars with maleic anhydride or succinic anhydride, condensates of hydroxycarboxylic acids with maleic anhydride or succinic anhydride, CMOS and organic acid salts of Bulder M and the like,

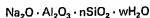
9) aluminosilicate salts:

No. 1 Crystalline aluminosilicate salts of the formula:



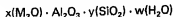
- 20 wherein M' represents an alkali metal atom, M'' represents an alkali earth metal atom exchangeable with calcium, x' , y' and w' represent mol numbers of the respective components and generally, x' is 0.7—1.5, y' is 0.6—6 and w' is a positive number,

No. 2 compounds of the following general formula are preferred as detergent builders:



- 25 wherein n represents a number of 1.8—3.0 and w represents a number of 1—6,

No. 3 Amorphous aluminosilicate salts of the formula:



wherein M represents a sodium and/or potassium atom, and x , y and w represent mol numbers of the respective components within the following ranges:

- 30 $0.7 \leq x \leq 1.2$ 30
 $1.6 \leq y \leq 2.8$

w : any positive number including 0, and

No. 4 amorphous aluminosilicate salts of the formula:



- 35 wherein M represents Na or K, and X , Y , Z and ω represent mol numbers of the respective components within the following ranges: 35

$$0.20 \leq X \leq 1.10$$

$$0.20 \leq Y \leq 4.00$$

$$0.001 \leq Z \leq 0.80$$

- 40 μ : any positive number including 0. 40

[2] Alkalis or inorganic electrolytes

The composition may contain 1—50 wt%, preferably 5—30 wt%, based on the composition, of one or more alkali metal salts of the following compounds as the alkalis or inorganic electrolytes:

- 45 silicates, carbonates and sulfates as well as organic alkalis such as triethanolamine, diethanolamine, monoethanolamine and triisopropanolamine. 45

V. Antiredeposition agents

The composition may contain 0.1—5% of one or more of the following compounds as antiredeposition agents: polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone and carboxymethylcellulose.

Among them, a combination of carboxymethylcellulose or/and polyethylene glycol with the cellulase of the present invention exhibits a synergism in removing muddy dirt.

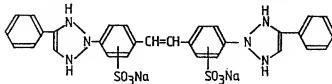
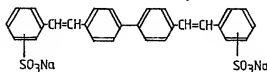
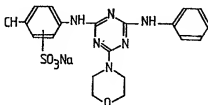
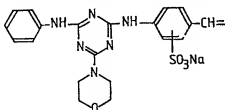
For preventing the decomposition of carboxymethylcellulose by the cellulase in the detergent, it is desirable that carboxymethylcellulose is granulated or coated before the incorporation in the composition.

VI. Bleaching agents

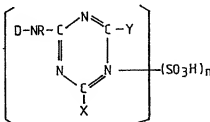
The use of the cellulase of the present invention in combination with a bleaching agent such as sodium percarbonate, sodium perborate, sodium sulfate/hydrogen peroxide adduct and sodium chloride/hydrogen peroxide adduct or/and a photo-sensitive bleaching dye such as zinc or aluminum salt of sulfonated phthalocyanine further improves the deterging effects.

VII. Bluig agents and fluorescent dyes

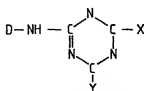
Various bluing agents and fluorescent dyes may be incorporated in the composition, if necessary. For example, compounds of the following structures are recommended:



Bluing agents of the following formula:



- wherein D represents a residue of a blue or purple, monoazo, disazo or anthraquinone dyestuff, X and Y each represent a hydroxyl group, amino group, an aliphatic amino group which may be substituted with a hydroxyl, sulfonic acid, carboxylic acid or alkoxyl group, or an aromatic or alicyclic amino group which may be substituted with a halogen atom or hydroxyl, sulfonic acid, carboxylic acid, lower alkyl or lower alkoxyl group, R represents a hydrogen atom or lower alkyl group excluding cases wherein (1) R represents the hydrogen atom and both X and Y represent hydroxyl or alkanolamino group at the same time and (2) R represents the hydrogen atom and one of X and Y represents the hydroxyl group and the other represents an alkanolamino group, and n represents an integer of at least 2,



wherein D represents a residue of a blue or purple, azo or anthraquinone dyestuff, and X and Y represent the same or different alkanolamino group or hydroxyl group.

VIII. Caking inhibitors

- 5 The following caking inhibitors may be incorporated in the powdery detergent: p-toluenesulfonic acid salts, xylenesulfonic acid salts, acetic acid salts, sulfosuccinic acid salts, talc, finely pulverized silica, clay, calcium silicate (such as Micro-Cell of Johns Manville Co.), calcium carbonate and magnesium oxide. 5

IX. Masking agents for factors inhibiting the cellulase activity

- 10 The cellulases are deactivated in some cases in the presence of copper, zinc, chromium, mercury, lead, manganese or silver ions or their compounds. Various metal chelating agents and metal-precipitating agents are effective against these inhibitors. They include, for example, divalent metal ion sequestering agents as listed in the above item [1] with reference to optional additives as well as magnesium silicate and magnesium sulfate. 10

- 15 Cellobiose, glucose and gluconolactone act sometimes as the inhibitors. It is preferred to avoid the co-presence of these saccharides with the cellulase as far as possible. In case the co-presence is unavoidable, it is necessary to avoid the direct contact of the saccharides with the cellulase by, for example, coating them. 15

- 20 Long-chain-fatty acid salts and cationic surfactants act as the inhibitors in some cases. However, the co-presence of these substances with the cellulase is allowable if the direct contact of them is prevented by some means such as tableting or coating. 20

The above-mentioned masking agents and methods may be employed, if necessary, in the present invention.

X. Cellulase-activators

- 25 The activators vary depending on variety of the cellulases. In the presence of proteins, cobalt and its salts, magnesium and its salts, and calcium and its salts, potassium and its salts, sodium and its salts or monosaccharides such as mannose and xylose, the cellulases are activated and their deterging powers are improved remarkably. 25

XI. Antioxidants

- 30 The antioxidants include, for example, tert-butyl-hydroxytoluene, 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 2,2'-butylidenebis(6-tert-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1-bis(4-hydroxyphenyl)cyclohexane. 30

XII. Solubilizers

- 35 The solubilizers include, for example, lower alcohols such as ethanol, benzenesulfonate salts, lower alkylbenzenesulfonate salts such as p-toluenesulfonate salts, glycols such as propylene glycol, acetylbenzenesulfonate salts, acetamides, pyridinedicarboxylic acid amides, benzoate salts and urea. 35

The detergent composition of the present invention can be used in a broad pH range of from acidic to alkaline pH.

- 40 The following examples will further illustrate the present invention. Unless otherwise stated, percentages in the following examples are given by weight. 40

Example 1

Deterging tests of various combinations of surfactant and cellulase on pieces of cotton cloth artificially stained with oil, fat and carbon were carried out.

45	1) Detergent composition:		45
	Surfactant	20%	
	Beef tallow soap	2%	
	Sodium tripolyphosphate	20%	
	Sodium silicate	10%	
50	Sodium carbonate	10%	
	Polyethylene glycol (average molecular weight: \overline{MW} 6000)	1%	50
	Fluorescent dye	0.4%	
	Water	10%	
	Enzyme	3%	
55	Glauber's salt	23.8%	
	Total	100%	55

2) Cloth artificially stained with oil and fat:

A cotton calico stained with the following oil, fat and carbon:

Oil composition (colored with carbon black) used for preparing the artificially stained cloth:

5	Cotton seed oil	60%	5
	Cholesterol	10%	
	Oleic acid	10%	
	Palmitic acid	10%	
	Liquid and solid paraffins	10%	

3) Deterging conditions and method and appraisal:

- 10 A detergent was dissolved in 4°DH hard water to obtain 1l of 0.133% aqueous detergent solution. Five pieces of the cotton cloth artificially stained with the oily dirt were immersed in the aqueous detergent solution. After leaving them to stand at 40°C for 2 hours, the detergent solution and the pieces of artificially stained cloth were transferred in a stainless steel beaker for Turgotometer and stirred at 100 rpm at 20°C for 10 minutes in the Turgotometer. After washing with running water, they were pressed with an iron and their reflectivities were measured. The deterging rate was calculated according to the following formula: 15

- 20 Reflectivities of the original cloth before the washing and those of the stained cloth before and after the washing were measured at 550 mμ by means of an automatic recording colorimeter (a product of Shimadzu Seisaku-sho) and the deterging rate (%) was calculated according to the following formula: 20

$$\text{Deterging rate (\%)} = \frac{\left(\begin{array}{c} \text{Reflectivity} \\ \text{after washing} \end{array} \right) - \left(\begin{array}{c} \text{Reflectivity} \\ \text{before washing} \end{array} \right)}{\left(\begin{array}{c} \text{Reflectivity of} \\ \text{original cloth} \end{array} \right) - \left(\begin{array}{c} \text{Reflectivity} \\ \text{before washing} \end{array} \right)} \times 100$$

An average of five samples were shown in Table 1.

4) Enzymes used:

- 25 (1) Cellulase-Onozuka (Kinki Yakult Co., Ltd.; obtained from *Trichoderma viride*; 4000 unit/g),
 (2) Cellulolin AP (Ueda Kagaku Co., Ltd.; obtained from *Aspergillus niger*, 860 unit/g),
 (3) Meicelase (Meiji Seika Co., Ltd.; obtained from *Trichoderma honingi*; 1100 unit/g),
 (4) Bacterial α-amylase (NOVO Co.; Termamyl 60 G; 60 KNU/g),
 (5) Amyloglucosidase (NOVO Co.; ANG; 200 AG/ml),
 (6) β-Glucanase (NOVO Co.; Celleflo 200L; 200 BGU/g),
 (7) Dextranase (NOVO Co.; DN25L; 25 KDU/g),
 (8) Galactomannase (NOVO Co.; Gamanase 1.5L; 1500 KVHCU/g),
 (9) Glucose-isomerase (NOVO Co.; Sweetzyme type A),
 (10) Bacterial protease (NOVO Co.; Alkalase 2.0 M, 2AU/g),
 (11) Bacterial protease (Gist Brocades Co.; Maxatase P; 330,000 DU/g),
 (12) Mould lipase (Nagase Sangyo Co.; Olipase) 35

5) Surfactants:

- (a) Sodium n-dodecylbenzenesulfonate
 (b) Sodium alkyl sulfate of oxoalcohol series (C₁₄₋₁₅)
 (c) Sodium alkyl ethoxy (P=3) sulfate of oxoalcohol series (C₁₄₋₁₅),
 (d) Sodium α-olefinsulfonate (C₁₈₋₁₉),
 (e) Sodium alkane (C₁₈) sulfonate,
 (f) Sec. Alcohol (C=13.5) ethoxylate
 (Average mol number of ethylene oxide added: EO=7),
 (g) Laurylbetaine
 (h) Laurylamine oxide,
 (i) Beef tallow soap, and
 (j) Mono (long-chain alkyl (of beef tallow)) trimethylammonium chloride. 45

6) Results:

	Detergent No.	Enzyme No.	Surfactant No.	Deterging rate (%)	
5	1	not used (balanced with Na_2SO_4)	a	70	5
	2*	1	a	85	
	3*	2	a	80	
	4*	3	a	82	
10	5	4	a	70	10
	6	5	a	70	
	7	6	a	69	
	8	7	a	70	
	9	8	a	70	
15	10	9	a	70	15
	11	10	a	70	
	12	11	a	70	
	13	12	a	70	
	14	1	not used (balanced with Na_2SO_4)	40	
20	15*	1	b	85	20
	16*	1	c	87	
	17*	1	d	86	
	18*	1	e	86	
25	19*	1	f	90	25
	20*	1	g	80	
	21*	1	h	85	
	22	1	i	65	
	23	1	j	68	
30	Note) Symbol * indicates the present invention and the others are referential examples.				30

The above results indicate that the specific combinations of surfactant (anionic, nonionic or ampholytic) with cellulase exhibit excellent deterging effects.

Example 2

1) Detergent compositions:

- 35 The same composition as in Example 1 was employed except that surfactant (a) was used and that no enzyme was used (balanced with Glauber's salt). 35

2) Cloth artificially stained with oil and fat, deterging conditions, deterging method and appraisal:

They were the same as in Example 1.

- 40 3) Cellulase used: 40
Snail cellulase (Disererase) (13):

- A cellulase extracted from a digestive canal of *Helix pomatia* according to a method shown in F. L. Mayers and D. H. Northcote, *Biochem. J.* 71, 749 (1959) was subjected to the test. The cellulase was prepared as follows: The digestive canal of *Helix pomatia* including the contents thereof was cut into a length of 1—2 cm while cooling with ice. An equal quantity of cold water was added thereto. The whole was treated with a homogenizer at 200 rpm for 30 s five times at intervals of 2 min. After centrifugal precipitation at 40°C for 30 min (19000 g), the resulting supernatant liquid was dialyzed in a dialysis cellophane tube for 16 h and then freeze-dried to obtain the cellulase. 45

- The thus obtained snail cellulase had a carboxymethylcellulose-decomposing activity (CMCase activity) of 0.08 unit/mg solid (1 unit/mg solid indicates a capacity of forming 1.0 μ mol of glucose from CMC in one hour at 37°C at pH 5) and a cotton cloth-decomposing activity of 5 unit/g solid. 50

Cellulosin AP (2) (shown in Example 1):

Cellulosin AP (2) had a CMCase activity of 0.8 unit/g solid.

4) Results:

	Detergent No.	Enzyme No.	Amount	Cotton cloth-decomposing activity (unit/kg detergent)	Deterging rate	
5	24	not used	0	0	70%	
	25*	2	0.1%	860	73%	
	26*	2	3%	25800	80%	
	27*	2	20%	172000	90%	
10	28	13	17.2%	860	70%	10
	29	13	25%	1250	70%	

Note) Symbol * indicates the present invention and the others are referential examples.

The above results suggest that a cellulase produced from an animal does not contribute to the deterging effect, that a cellulase produced from a bacterium or fungi should have an enzymatic activity higher than a given value for exhibiting the deterging effect and that the latter cellulase should be contained in at least a given amount in 1 kg of the detergent.

Example 3

1) Detergent composition:

	Sodium n-dodecylbenzenesulfonate	10 wt.%	
20	Sodium α -olefinsulfonate (C ₁₄₋₁₈)	3	20
	Sodium alkyl sulfate (C ₁₄₋₁₈)	3	
	Sodium alkyl (C ₁₄₋₁₈) ethoxy (1.5 mol) sulfate	2	
	Alkyl (C ₁₈₋₁₉) ethoxylate (15 mol)	2	
	Soap (sodium salt of tallow fatty acid)	2	
25	Non-phosphate type builder or sodium tripolyphosphate	0 or 20	25
	Cellulase [Cellulase (1) as used in Example 1]	0 or 3	
	Sodium silicate	10	
	Sodium carbonate	10	
	Carboxymethylcellulose	1	
30	Polyethylene glycol	1	30
	Fluorescent dye	0.4	
	Sodium p-toluenesulfonate	2	
	Water	5 wt.%	
	Glauber's salt	balance	
35	Total	100	35

2) Mud-stained cloths (artificially stained cloths):

Kanuma sekigyoku soil for horticultural use was dried at 120°C±5°C for 4 h and then pulverized. 150 mesh (100 μ m)-passed soil particles were dried at 120°C±5°C for 2 h. 150 g of the soil particles was dispersed in 1000 l of Perclene. A calico #2023 was contacted with the dispersion and brushed. After removal of the dispersion, excessive mud remaining on the cloth was removed (Japanese Patent Laid-Open No. 26473/1980).

Test pieces having a size of 10 cm x 10 cm were prepared and subjected to the tests.

3) Deterging conditions and method and appraisal:

Reflectivities of the original cloth and those of the mud-stained cloth before and after the washing were measured at 460 m μ .

The others were the same as those in Example 1.

4) Non-phosphate builders and sodium tripolyphosphate used:

	(a) Sodium nitrilotriacetate,		
	(b) Sodium ethylenediaminetetraacetate,		
50	(c) Sodium diglycolate,		50
	(d) Sodium hydroxydisuccinate,		
	(e) Sodium carboxymethylhydroxysuccinate,		
	(f) Sodium carboxymethyltartronate,		
	(g) Sodium malate,		
55	(h) Sodium tartrate,		55
	(i) Sodium citrate,		
	(j) Type 4A crystalline zeolite 4.5 hydrate,		

- (k) Sodium polyacrylate (\overline{MW} =3000),
 (l) Hydrolyzed and neutralized maleic anhydride/methyl vinyl ether copolymer [Gantretz AN 169 (GAF)]
 (m) Hydrolyzed and neutralized maleic anhydride/diisobutylene copolymer [Demol EP (a product of Kao Soap Co., Ltd.)],
 (n) Hydrolyzed and neutralized maleic anhydride/pentene copolymer (\overline{MW} =2000),
 (o) Sodium carbonate, and
 (p) Sodium tripolyphosphate.

5) Results:

10	Detergent No.	Builder	Deterging rate		10
			Cellulase (1) not used (balanced with Na_2SO_4) (referential example)	used (present invention)	
15	30	not used	60	80	15
	31	a	81	92	
	32	b	78	88	
	33	c	71	79	
20	34	d	71	79	20
	35	e	72	82	
	36	f	72	82	
	37	g	71	80	
	38	h	72	79	
25	39	i	76	87	25
	40	j	78	88	
	41	k	76	88	
	42	l	77	87	
	43	m	77	87	
30	44	n	75	82	30
	45	o	72	82	
	46	p	80	—	

It is understood from the results that the present composition has an improved deterging power when it applies to a phosphate builder-free detergent.

35 Example 4

1) Detergent compositions:

35		(A)	(B)	35
		—	15	
	Triethanolamine salt of n-dodecylbenzenesulfonate	—	15	
	Sodium alkyl (C_{12-13}) ethoxy (3 mol) sulfate	25	—	
	Sec. alcohol ($\text{C}=13.5$) ethoxylate ($\text{EO}=7$)	25	10	
40	Coconut fatty acid diethanolamine	—	2	40
	Polyethylene glycol	3	1	
	Sodium citrate	—	10	
	Sodium m-xylenesulfonate	—	5	
	Triethanolamine	5	2	
45	Fluorescent dye (Tinopal CBS-X; a product of Ciba-Geigy Co.)	0 or 0.5	0.5	45
	Blueing agent	0.05	—	
	Ethyl alcohol	8	8	
	Water	Balance	Balance	
50	Perfume	0.1	0.1	50
	Cellulase (cellulase (1) in Example 1)	0 or 2	0 or 2	
Total		100	100	

2) Deterging power tests using fluorescent dye-containing detergent compositions A and B;

2—1) Naturally stained collar neck cloths:

- 55 Cotton cloths were sewed on collar necks of shirts. Male adults were asked to wear the shirts for two days. Cloths having symmetrical stain distributions about the center of the cloth were selected and cut in halves at said center. The halves were subjected to the test.

2—2) Deterging conditions and method:

In the deterging test of the naturally stained cloths, each of these cloths having a size of 9×30 cm was cut into halves at the axis of symmetry. One of a pair of the stained cloth (9×15 cm) was washed using a cellulase-free detergent (standard) and the other was washed with the detergent of the present invention (comparative). 10 pieces of the naturally stained cloths were immersed in 1 l of the detergent solution and treated with a Turgotometer at 100 rpm for 10 min, dried and subjected to the judgement.

2—3) Appraisal method:

A pair of the above right and left halves obtained from the same, symmetrically stained sample and washed with the standard detergent and comparative detergent, respectively, was judged macroscopically. The thus treated cloths were ranked based on 10 standard ranks of strain. Deterging power of the standard detergent was expressed as 100. (A difference of 1 in the values indicates that a significant difference is recognized between the samples macroscopically).

3) Brightening tests using composition A:**3—1) Washing conditions:**

Clothes: 10 new knit underwears of 100% cotton or 4 new shirts of blended fiber of polyester/cotton.

Washing method: 20 cc of liquid detergent was dissolved in 5 l of city water and the clothes were immersed therein at an initial temperature of 40°C. Two hours after, city water at room temperature was added thereto to make the total quantity 30 l. The washing was effected by means of an ordinary washing machine provided with a stirring pulsator for 10 min. After completion of the washing, the clothes were dehydrated by means of a dehydrator for one min. The thus dehydrated clothes were washed with 30 l of city water for 3 min in the washing machine. The washing with 30 l of fresh city water was repeated once. The clothes were dried with an electric drier. The above-mentioned washing cycle was repeated 50 times and brightnesses (whitenesses) of the clothes were judged.

3—2) Judgement of brightness (whiteness):

Fluorescent dyes contained in detergents for clothes generally absorb a light of 380 nm and they emit a fluorescent light having a peak at 430—440 nm. Therefore, if a xenon lamp is used as a light including U.V. rays, the fluorescent strength (whiteness) can be represented by Z having the maximum excitation at 440 nm in distribution coefficients of X, Y and Z. Accordingly, the amounts of the fluorescent dye fixed on the clothes were determined by measuring Z value by means of a Xenon Digital Colorimetric Color-Difference Meter (a product of Suga Shiken-ki Co., Ltd.).

4) Results:**4—1) Deterging power for collar necks:**

Composition A (cellulase-free): Composition A (containing cellulase)=100:103

Composition B (cellulase-free): Composition B (containing cellulase)=100:103

It is noted from results in Examples 1, 3 and 4—1 that the present composition has a deterging effect to cellulose fabric despite of the kind of soils.

4—2) Whiteness of clothes after washing 50 times (Composition A):

	Before Washing	Cellulase-free	Cellulase added
Cotton knit underwears	10.5±0.05	7.4±0.1	8.2±0.1
Shirts made of blended fiber of polyester/cotton (65/35)	7.4±0.1	6.0±0.1	7.1±0.1

It is said from Example 4—2 that the composition of the present invention is improved in whiteness effect by a fluorescent dye.

Example 5**1) Detergent compositions:**

	A (powdery detergent)	B (powdery detergent)	
5	10%	10	5
Sodium n-dodecylbenzenesulfonate	3	3	
Sodium alkyl sulfate (C_{12-15})	2	2	
Sodium alkylethoxysulfate (C_{12-15} , EO=1.5)	5	5	
Sodium α -olefinsulfonate (C_{12-15})	2	2	
10 Soap (tallow fatty acid sodium salt)	10	10	10
Sodium tripolyphosphate	10	10	
Crystalline sodium aluminosilicate (type 4A)	10	10	
Sodium silicate	10	10	
Sodium carbonate	1	1	
15 Carboxymethylcellulose	1	1	15
Polyethylene glycol (MW=6000)	0.4%	0.4	
Fluorescent dye	2	2	
Sodium p-toluenesulfonate	10	10	
Water	10.6	Balance	
20 Glauber' salt	3	3	20
Enzyme	10	0.005	
Bleaching agent			
Total	100%	100%	

2) Artificially stained cloth used:

- 25 EMPA 112;
Cotton test pieces (10 cm x 10 cm) stained with cocoa were prepared and subjected to the tests. 25

3) Deterging and bleaching conditions and method:

- The deterging bleaching agent was dissolved in 4°DH hard water to prepare 1 l of 0.5% aqueous solution. Five pieces of EMPA 112 cotton cloth artificially stained were added to the above-obtained aqueous solution. After leaving them at 40°C for 2 h (when composition B was used, they were left under irradiation with natural light), the solution and the artificially stained clothes were directly transferred in a stainless steel beaker for a Turgotometer and stirred at 100 rpm at 20°C for 10 minute in the Turgotometer. After washing with running water, they were pressed with an iron and their reflectivities were measured. The deterging rate was calculated according to the following formula:
- 35 Reflectivities of the original cloth before the washing and bleaching and those of the stained cloth before and after the washing and bleaching were measured at 460 m μ by means of an automatic recording colorimeter (a product of Shimadzu Seisaku-sho) and the deterging and bleaching rate (%) was calculated according to the following formula:

$$\text{Deterging and bleaching rate (\%)} = \frac{\left(\begin{array}{c} \text{Reflectivity} \\ \text{after washing} \\ \text{and bleaching} \end{array} \right) - \left(\begin{array}{c} \text{Reflectivity} \\ \text{before washing} \\ \text{and bleaching} \end{array} \right)}{\left(\begin{array}{c} \text{Reflectivity} \\ \text{of original} \\ \text{cloth} \end{array} \right) - \left(\begin{array}{c} \text{Reflectivity} \\ \text{before washing} \\ \text{and bleaching} \end{array} \right)} \times 100$$

- 40 An average of five samples was shown in the following table. 40

4) Enzymes used:

- (1) Not used.
(2) Cellulosin AP (a product of Ueda Kagaku Co., Ltd.)
(3) Cellulase-Onozuka enzyme (1) in Example 1

- 45 5) Bleaching agent used: 45

- (a) Not used (balanced with Glauber's salt),
(b) Sodium percarbonate (a product of Nihon Peroxide Co.)
(c) Sodium perborate (a product of Mitsubishi Gas Kagaku Co.)
(d) Aluminum salt of sulfonated phthalocyanine (a product of CIBA-GEIGY Co.), and
50 (e) Thiourea dioxide (a product of Tokai Denka Co.) 50

6) Results of the measurement of deterging and bleaching power of artificially stained EMPA 112 cloth:

Table 1

5	<i>Enzyme and bleaching agent in detergent</i>		<i>Deterging and bleaching power</i>		5
			<i>Composition A</i>	<i>Composition B</i>	
10	1	a	40	40	10
		b	50	—	
		c	50	—	
		d	—	46	
		e	46	—	
15	2	a	46	46	15
		b*	58	—	
		c*	58	—	
		d*	—	54	
		e*	54	—	
20	3	a	48	48	20
		b*	60	—	
		c*	60	—	
		d*	—	56	
		e*	56	—	

Note) Symbol * indicates the present invention and the others are referential examples.

It is understood from the above that the present composition has a synergistic effect in respect to deterging and bleaching effect by use of cellulase and a bleaching agent.

25 Example 6

1) Detergent composition:

Composition A in Example 5 containing sodium percarbonate 5)—(b).

2) Cloths stained with complex dirt:

The naturally stained collar cloths [Example 4—2—1)].

30 3) Deterging conditions and method:

The deterging conditions and method were the same as in Example 4—2—2) except that the cloths were immersed in a 0.5% deterging solution at 40°C for 2 h, then city water was added to the solution to contain detergent concentration to 0.133% before the washing with the Turgotometer.

4) Appraisal method:

The appraisal method was the same as that shown in Example 4—2—3).

5) Enzymes used:

(1) Not used (balanced with Glauber's salt).

(2) Cellulase [Cellulase-Onozuka; Example 1—(1)]

(3) Above cellulase (2)/lipase (a product of Gist Brocades Co.; produced from *R. oryzae*)=1:1.

(4) Cellulase (2)/amylase (termamyl 60 G; a product of NOVO Industries Co.)=1:1.

(5) Cellulase (2)/protease (alkalase 2.0 M; a product of NOVO Industries Co.)=1:1.

(6) Cellulase (2)/protease/lipase=2:1:1.

(7) Cellulase (2)/protease/amylase=2:1:1

(8) Cellulase (20)/protease/lipase/amylase=3:1:1:1.

6) Results:

	<i>Enzyme in detergent</i>	<i>Deterging power index</i>	
	1 not used	100	
	2*	102	
5	3*	103.5	5
	4*	103.5	
	5*	105	
	6*	105	
	7*	105	
10	8*	105	10

Note) Symbol * indicates the present invention and the others are referential examples.

It is understood from the above results that the combination of the cellulase with other enzymes such as protease, lipase or amylase removes the complex dirt effectively.

Claims

- | | | |
|----|--|----|
| 15 | 1. A detergent composition for clothing containing:
(a) at least one surfactant selected from anionic surfactants, and ampholytic surfactants, and
(b) a bacteria- and/or fungi-derived cellulase having an enzyme activity as herein defined of at least 100 units for cotton fabric. | 15 |
| 20 | 2. A composition according to Claim 1 wherein the surfactant content of the composition is at least 5 wt.%.
3. A composition according to Claim 1 wherein the cellulase content of the composition is such that 1 kg of the composition has an enzyme activity towards cotton fabric of at least 100 units. | 20 |